Improved ceria catalysts via doping and graphene oxide templating strategies

Shawn Rood[a,b], **Anais Gomez**[b], **Laura Torrente-Murciano**[c], **Salvador Eslava**[b]*
[a]*Centre for Sustainable Chemical Technologies, University of Bath, Bath, BA2 7AY, UK*
[b]*Department of Chemical Engineering, University of Bath, Bath, BA2 7AY, UK*
[c]*Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, CB3 0AS, UK*
**Corresponding author: S.Eslava@bath.ac.uk*

Abstract: Two limitations of current automotive three-way catalysts are poor low-temperature catalytic activity and gradual degradation of performance due to sintering at very high temperatures. In this work, two strategies to resolve these issues are explored. Doped ceria nanorods are shown to have improved low-temperature activity for both CO oxidation and NO reduction, with a two-dopant catalyst demonstrating good performance for both reactions. For high-temperature exposure, the use of graphene oxide as a sacrificial template in ceria synthesis produces a ceria nanoflake catalyst with enhanced sintering resistance and better retention of surface area at high temperatures.
Keywords: Ceria, emissions, graphene oxide

1. Introduction

Ceria is an important component in automotive three-way catalysis, but pure ceria alone is not effective at removing harmful pollutants from vehicle exhaust. In a typical three-way automotive catalyst, the active catalyst is platinum group metal (PGM) particles dispersed over a ceria-containing washcoat. However, at very low temperatures, catalytic converters are not active, so emitted pollutant levels are elevated during the first few minutes of vehicle operation.[1] At very high temperatures, metal particle catalysts gradually sinter over the lifetime of a vehicle, leading to loss of surface area and catalytic activity.[2]

Herein, two approaches are explored to mitigate these issues. In this work, a template free hydrothermal method is utilized to synthesize doped ceria nanorods. Doping ceria with other metals is a strategy that can be used to improve low temperature catalytic activity. Ceria nanorods are an ideal morphology for three-way catalysis because they selectively expose the (110) crystal surface, known to have a higher percentage of surface oxygen vacancies and improved activity for oxidative reactions.[3] In the second approach, graphene oxide (GO) is used as a sacrificial template for the synthesis of two-dimensional ceria nanoflakes. When calcined at high temperatures, these nanoflakes demonstrate improved textural and catalytic properties compared with similarly prepared untemplated ceria.

2. Experimental

Ceria nanorods were prepared via hydrothermal synthesis.[3] Cerium nitrate and a dopant precursor were added to a NaOH solution and heated in an autoclave at 100 °C for 10 hours, then filtered and dried.

Ceria nanoflakes were prepared with a room-temperature precipitation method in an ammonia solution at pH 11, using graphene oxide prepared with a modified Tour *et al*. synthesis.[4] The product was calcined in air at 400 °C to remove the GO, followed by subsequent higher-temperature calcinations if necessary.

Catalytic activity tests for CO oxidation and NO reduction were performed in a U-shaped quartz tube reactor at atmospheric pressure. 15 mg of ceria catalyst was dispersed in a 4 cm^3 bed of silicon carbide particles. Tests were conducted between room temperature and 500 °C with a flow rate of 50 mL min^{-1}.

3. Results and discussion

Copper and chromium-doped ceria nanorods were hydrothermally synthesized with different dopant levels to compare with undoped ceria nanorods. TEM micrographs (Figure 1a) show nanorods a wide range of sizes, with nanorod widths generally below 50 nm and lengths ranging from 100 to several hundred nm. For CO oxidation, improved low-temperature catalytic activity was observed for Cu-doped ceria nanorods, but not Cr-doped ceria nanorods. The reverse was true for NO reduction. A dual-doped Cu/Cr/ceria nanorod catalyst demonstrated improved performance for both CO oxidation and NO reduction (Figure 1b-c).

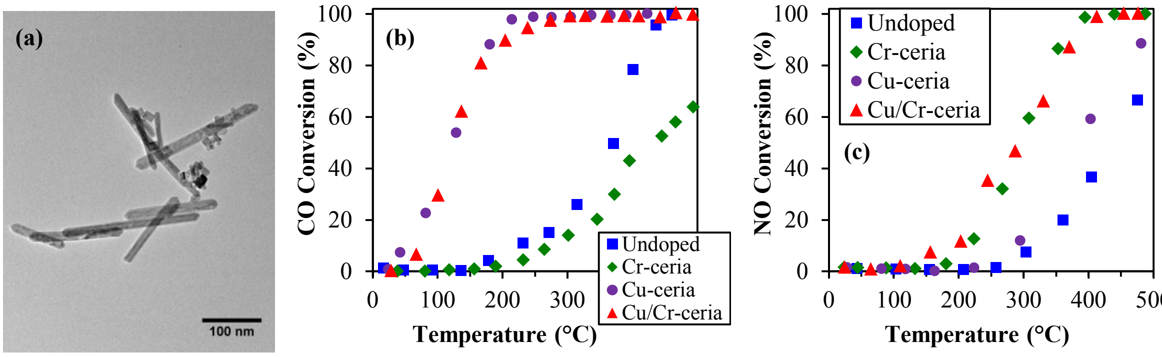

Figure 1. (a) TEM micrograph of hydrothermally synthesized copper-doped ceria nanorods. (b) CO oxidation and (c) NO reduction catalytic activity for undoped and doped ceria nanorod catalysts.

Untemplated ceria particles and graphene oxide-templated ceria flakes were prepared via precipitation synthesis. As shown in Figure 2a, the two-dimensional morphology of GO was successfully replicated with ceria crystallites, in contrast to the large agglomerations from the untemplated synthesis. Although both samples lose surface area upon calcination at high temperatures, the GO-templated ceria nanoflakes demonstrated improved resistance to sintering (Figure 2b).

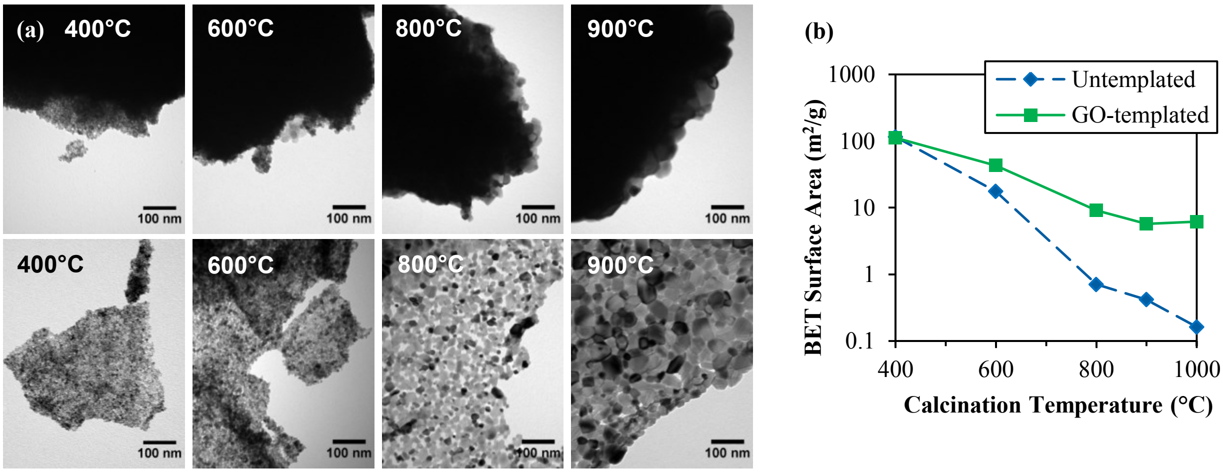

Figure 2. (a) TEM micrographs of (above) untemplated ceria and (below) GO-templated ceria, calcined at various temperatures. (b) BET surface area for untemplated ceria particles and GO-templated ceria nanoflakes vs. calcination temperature.

4. Conclusions

Doping the lattice structure of ceria nanorods offers a possible solution for the issue of low-temperature catalytic activity in three-way catalysts. Additionally, these catalysts are PGM-free, providing economic and sustainability benefits. In contrast, the use of graphene oxide as a sacrificial template for the production of ceria nanoflakes is a potential strategy for improving high-temperature sintering resistance in automotive catalysis. These strategies offer novel approaches for improving three-way catalysis for automotive emissions control, increasingly important as legal limits on emitted pollutants grow stricter in countries across the world.

References

1. C.H. Bartholomew, R.J. Farrauto, Fundamentals of Industrial Catalytic Processes, Wiley, Hoboken, 2006, p. 705-752.
2. J.-J. He, C.-X. Wang, T.-T. Zheng, Y.-K., Zhao, Johnson Matthey Technology Review, 60 (2016) 196-203.
3. J.M. López, A.L. Gilbank, T. García, B. Solsona, S. Agouram, L. Torrente-Murciano, Appl. Catal. B-Environ., 174 (2015) 403-412.
4. S. Eslava, A. Reynal, V.G. Rocha, S. Barg, E. Saiz, J. Mater. Chem. A, 19 (2016) 7200-7206.